

CLAIMS

WE CLAIM:

1. A photoinitiator system for a cationically polymerizable resin, the
5 photoinitiator system comprising:
(a) an iodonium salt;
(b) a visible light sensitizer; and
(c) an electron donor compound having an oxidation potential greater
than 0 and less than that of 1,4-dimethoxybenzene when measured versus a saturated
10 calomel electrode;

wherein the photoinitiator system has a photoinduced potential less than that of 3-
dimethylaminobenzoic acid in a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium
hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

2. A photopolymerizable composition comprising:
(a) a cationically polymerizable resin; and
(b) a photoinitiator system for the cationically polymerizable resin, the
15 photoinitiator system comprising:
(i) an iodonium salt;
(ii) a visible light sensitizer; and
(iii) an electron donor compound having an oxidation potential
20 greater than 0 and less than that of 1,4-dimethoxybenzene when measured versus a
saturated calomel electrode; and

wherein the photoinitiator system has a photoinduced potential less than that of 3-
25 dimethylaminobenzoic acid in a standard solution of 2.9×10^{-5} moles/g diphenyl
iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

3. A photopolymerizable composition according to claim 2 wherein the
cationically polymerizable resin is selected from the group consisting of epoxy, oxetane,
30 vinyl ether and spiro-orthocarbonate resins, and combinations thereof.

4. A photopolymerizable composition according to claim 3 wherein the cationically polymerizable resin comprises an epoxy resin.

5. A photopolymerizable composition according to claim 4 wherein the cationically polymerizable resin comprises a silicon-containing epoxy resin.

6. A photopolymerizable composition according to claim 3 wherein the cationically polymerizable resin comprises a blend of a silicon-containing epoxy resin and an epoxy resin that does not contain silicon.

7. A photopolymerizable composition according to claim 2 wherein the iodonium salt is selected from the group consisting of diaryliodonium hexafluorophosphate, diaryliodonium hexafluoroantimonate, 4-octyloxyphenyl phenyliodonium hexafluoroantimonate, 4-(2-hydroxytetradecyloxyphenyl) phenyliodonium hexafluoroantimonate, 4-(1-methylethyl)phenyl 4-methylphenyliodonium tetrakis(pentafluorophenyl)borate, and combinations thereof.

8. A photopolymerizable composition according to claim 2 wherein the visible light sensitizer is selected from the group consisting of ketones, coumarin dyes, xanthene dyes, fluorone dyes, fluorescein dyes, aminoketone dyes, p-substituted aminostyryl ketone compounds, and combinations thereof.

9. A photopolymerizable composition according to claim 2 wherein the visible light sensitizer is an alpha-diketone.

10. A photopolymerizable composition according to claim 2 wherein the electron donor compound increases the polymerization speed of the photopolymerizable composition relative to the same composition but not containing an electron donor compound.

11. A photopolymerizable composition according to claim 2 wherein the electron donor compound is soluble in the photopolymerizable composition.

12. A photopolymerizable composition according to claim 2 wherein the electron donor compound does not absorb a significant amount of light at the wavelength of the light used to photopolymerize the composition.

13. A photopolymerizable composition according to claim 2 wherein the electron donor compound is substantially non-light absorbing at the wavelength at which the visible light sensitizer displays maximum light absorption.

14. A photopolymerizable composition according to claim 2 wherein the electron donor compound has a pK_b greater than 8.

15. A photopolymerizable composition according to claim 2 wherein the composition cures after less than about 2 minutes exposure to a light source that generates light of a wavelength to which the visible light sensitizer is sensitive.

16. A photopolymerizable composition according to claim 2 wherein the electron donor compound has an oxidation potential less than about 1.35 volts when measured using a saturated calomel electrode.

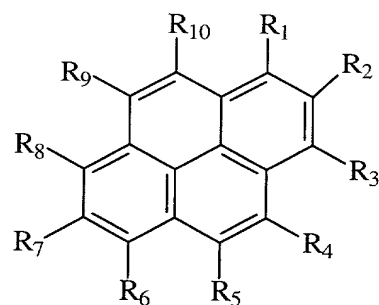
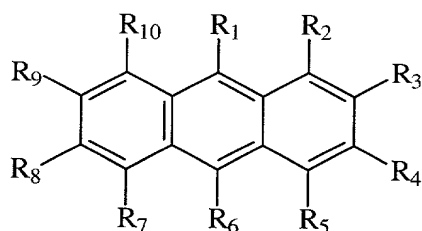
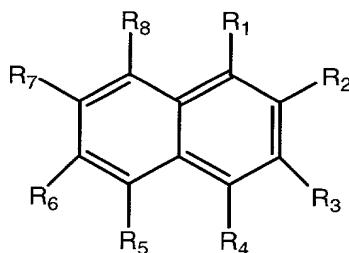
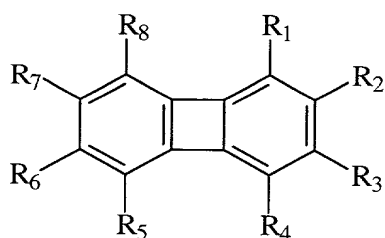
17. A photopolymerizable composition according to claim 16 wherein the electron donor compound has an oxidation potential between about 0.5 and 1.34 volts when measured using a saturated calomel electrode.

18. A photopolymerizable composition according to claim 2 wherein the electron donor compound is selected from the group consisting of polycyclic aromatic compounds and N-alkyl carbazole compounds.

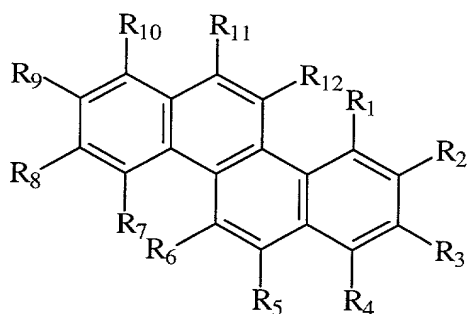
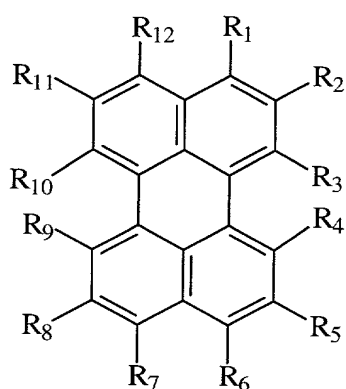
19. A photopolymerizable composition according to claim 2 wherein the polycyclic aromatic electron donor compound is selected from the group consisting of biphenylenes, naphthalenes, anthracenes, benzanthracenes, pyrenes, azulenes, pentacenes, decacyclenes, and derivatives and combinations thereof.

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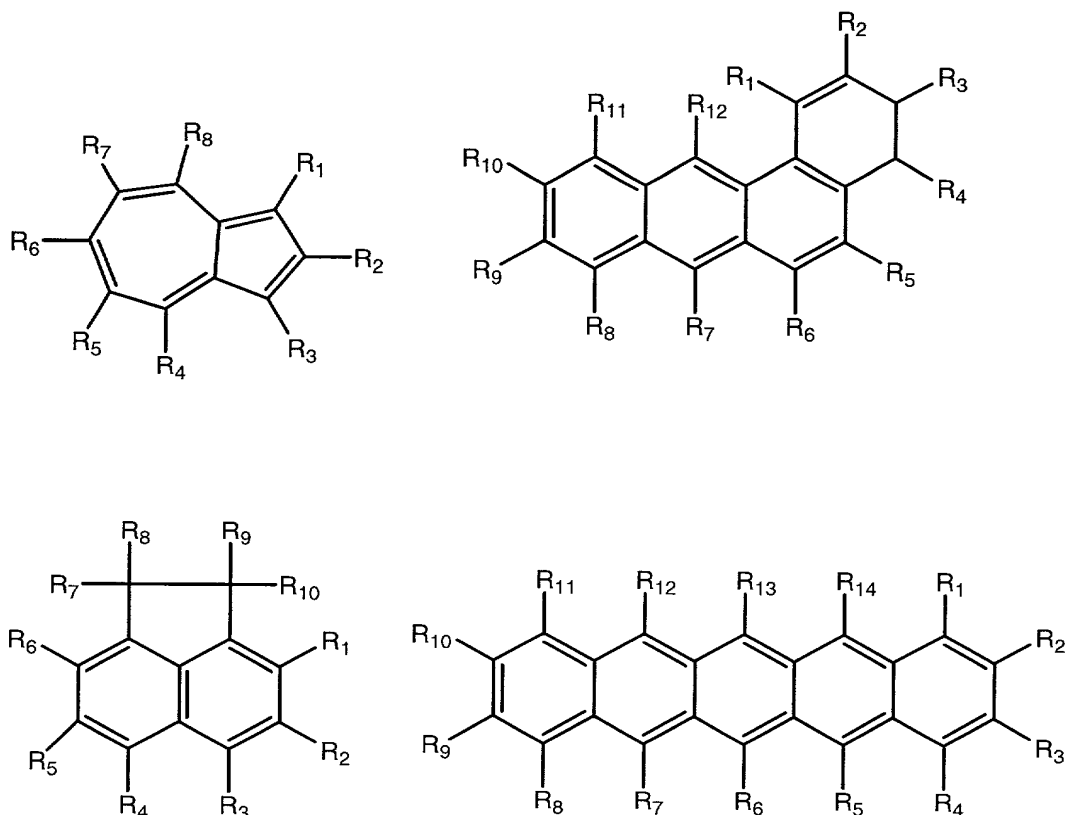
20. A photopolymerizable composition according to claim 2 wherein the electron donor compound is a polycyclic aromatic compound having one of the following structures:



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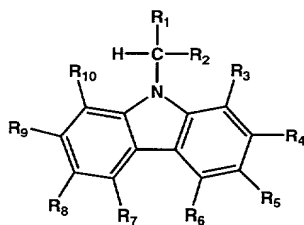


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wherein each of R_1 to R_{14} is independently selected from H, or alkyl or aromatic hydrocarbon groups, wherein the alkyl or aromatic hydrocarbon groups may be optionally substituted by one or more halogen, -CN, -OH, -SH, -COOH, -COOC₁₋₁₀ alkyl, -(C₁₋₁₀ alkyl)₀₋₁-COH, -(C₁₋₁₀ alkyl)₀₋₁-CO-C₁₋₁₀ alkyl, or -CO-C₁₋₁₀ alkyl groups, and further wherein any of R_1 to R_{14} may cooperate to form an aromatic or cycloalkyl ring.

21. A photopolymerizable composition according to claim 2 wherein the electron donor compound is an N-alkyl carbazole compound having the following structure:



wherein each R₁ to R₁₀ is independently selected from H, or alkyl or aromatic hydrocarbon groups, wherein the alkyl and aromatic hydrocarbon groups may be optionally substituted by one or more halogen, -CN, -OH, -SH, -COOH, -COOC₁₋₁₀ alkyl, -(C₁₋₁₀ alkyl)₀₋₁-COH, -(C₁₋₁₀ alkyl)₀₋₁-CO-C₁₋₁₀ alkyl, -CO-C₁₋₁₀ alkyl, and further wherein R₁ and R₁₀ may cooperate to form an aromatic, cycloalkyl or low basicity heterocyclic ring.

22. A photopolymerizable composition according to claim 2 further comprising a free-radically polymerizable resin.

23. A photopolymerizable composition according to claim 2 further comprising a hydroxyl-containing material.

24. A photopolymerizable composition according to claim 2 wherein the photopolymerizable composition is a photopolymerizable adhesive.

25. A photopolymerizable composition according to claim 2 wherein the photopolymerizable composition is a curable ink imaging layer, a silverless imaging layer, an imaging layer on a projection plate, or an imaging layer on a laser plate.

26. A photopolymerizable composition according to claim 2 wherein the photopolymerizable composition has been polymerized to provide a hard coat layer on an optical lens.

27. A photopolymerizable composition according to claim 2 wherein the photopolymerizable composition has been polymerized to provide a coating on an optical fiber.

28. A photopolymerizable dental material comprising:
(a) an epoxy resin; and
(b) a photoinitiator system for the epoxy resin, the photoinitiator system comprising:

(i) an iodonium salt;
(ii) a visible light sensitizer; and
(iii) a polycyclic aromatic electron donor compound having an oxidation potential greater than 0 and less than that of 1,4-dimethoxybenzene when measured versus a saturated calomel electrode; and

wherein the photoinitiator system has a photoinduced potential less than that of 3-dimethylaminobenzoic acid in a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

29. A photopolymerizable dental material according to claim 28 wherein the epoxy resin is a silicon-containing epoxy resin.

30. A photopolymerizable dental material according to claim 28 wherein the epoxy resin comprises a blend of a silicon-containing epoxy resin and an epoxy resin that does not contain silicon.

31. A photopolymerizable dental material according to claim 28 wherein the polycyclic aromatic electron donor compound is selected from the group consisting of biphenylenes, naphthalenes, anthracenes, benzanthracenes, pyrenes, azulenes, pentacenes, decacyclenes, and derivatives and combinations thereof.

32. A photopolymerizable dental material according to claim 31 wherein the visible light sensitizer is selected from the group consisting of ketones, coumarin dyes, xanthene dyes, fluorone dyes, and fluorescein dyes, and combinations thereof.

33. A photopolymerizable dental material according to claim 32 wherein the iodonium salt is selected from the group consisting of diaryliodonium

hexafluorophosphate, diaryliodonium hexafluoroantimonate, 4-octyloxyphenyl phenyliodonium hexafluoroantimonate, 4-(2-hydroxytetradecyloxyphenyl) phenyliodonium hexafluoroantimonate, 4-(1-methylethyl)phenyl 4-methylphenyliodonium tetrakis(pentafluorophenyl)borate, and combinations thereof.

34. A photopolymerizable dental material according to claim 28 wherein the photopolymerizable dental material further comprises a free-radically polymerizable resin.

35. A photopolymerizable dental material according to claim 28 wherein the photopolymerizable dental material further comprises a hydroxyl-containing material.

36. A photopolymerizable dental material comprising:

- (a) an epoxy resin; and
- (b) a photoinitiator system for the epoxy resin, the photoinitiator system comprising:
 - (i) an iodonium salt;
 - (ii) a visible light sensitizer; and
 - (iii) an N-alkyl carbazole electron donor compound having an oxidation potential greater than 0 and less than that of 1,4-dimethoxybenzene when measured versus a saturated calomel electrode; and

wherein the photoinitiator system has a photoinduced potential less than that of 3-dimethylaminobenzoic acid in a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

37. A photopolymerizable dental material according to claim 36 wherein the epoxy resin is a silicon-containing epoxy resin.

38. A photopolymerizable dental material according to claim 36 wherein the epoxy resin comprises a blend of a silicon-containing epoxy resin and an epoxy resin that does not contain silicon.

39. A photopolymerizable dental material according to claim 36 wherein the N-alkyl carbazole electron donor compound is N-methyl carbazole.

40. A photopolymerizable dental material according to claim 39 wherein the visible light sensitizer is selected from the group consisting of ketones, coumarin dyes, xanthene dyes, fluorone dyes, and fluorescein dyes, and combinations thereof.

41. A photopolymerizable dental material according to claim 40 wherein the iodonium salt is selected from the group consisting of diaryliodonium hexafluorophosphate, diaryliodonium hexafluoroantimonate, 4-octyloxyphenyl phenyliodonium hexafluoroantimonate, 4-(2-hydroxytetradecyloxyphenyl) phenyliodonium hexafluoroantimonate, 4-(1-methylethyl)phenyl 4-methylphenyliodonium tetrakis(pentafluorophenyl)borate, and combinations thereof.

42. A photopolymerizable dental material comprising:
(a) an epoxy resin; and
(b) a photoinitiator system for the epoxy resin, the photoinitiator system comprising:

(i) an iodonium salt selected from the group consisting of diaryliodonium hexafluorophosphate, diaryliodonium hexafluoroantimonate, 4-octyloxyphenyl phenyliodonium hexafluoroantimonate, 4-(2-hydroxytetradecyloxyphenyl) phenyliodonium hexafluoroantimonate, 4-(1-methylethyl)phenyl 4-methylphenyliodonium tetrakis(pentafluorophenyl)borate, and combinations thereof;

(ii) an alpha-diketone visible light sensitizer; and
(iii) an electron donor compound selected from the group consisting of biphenylene, anthracene, 9-methylantracene, 9-vinyl anthracene, 9-phenylantracene, 9,10-diphenylantracene, 9,10-dimethylantracene, 2-ethylantracene, acenaphthene, pyrene, pentacene, decacyclene, azulene, 7,12-dimethyl-1,2-benzanthracene, 1,2-benzanthracene, 1,4-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, N-methyl carbazole, and combinations thereof;

wherein the photoinitiator system has a photoinduced potential less than that of 3-dimethylaminobenzoic acid in a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

43. A photopolymerizable dental material according to claim 42 wherein the alpha-diketone visible light sensitizer is camphorquinone.

44. A photopolymerizable dental material according to claim 43 wherein the dental material is a dental adhesive or a dental composite.

45. A method of reducing the time needed to polymerize a cationically polymerizable resin, the method comprising the steps of:

- (a) providing a cationically polymerizable resin;
- (b) providing a photoinitiator system for the cationically polymerizable resin, the photoinitiator system comprising:
 - (i) an iodonium salt;
 - (ii) a visible light sensitizer; and
 - (iii) an electron donor compound having an oxidation potential greater than 0 and less than that of 1,4-dimethoxybenzene when measured versus a saturated calomel electrode; and

wherein the photoinitiator system has a photoinduced potential less than that of 3-dimethylaminobenzoic acid in a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone;

- (c) combining the cationically polymerizable resin and the photoinitiator system to provide a polymerizable mixture; and
- (d) exposing the polymerizable mixture to a light source having a wavelength and intensity to which the photoinitiator system is reactive and for a time until the polymerizable mixture attains a hard, tack-free state;

wherein the time until the polymerizable mixture attains a hard, tack-free state is less than the time required for the same polymerizable mixture, but excluding the electron

donor compound, to achieve the same hard, tack-free state when exposed to the same light source.